



A new process of lead recovery from waste lead-acid batteries by electrolysis of alkaline lead oxide solution

Junqing Pan ^{a,*}, Chao Zhang ^a, Yanzhi Sun ^{b,*}, Zihao Wang ^a, Yusheng Yang ^a

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^b National Fundamental Research Laboratory of New Hazardous Chemicals Assessment and Accident Analysis, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

This paper reports a new lead recovery method, in which high purity metallic Pb is directly produced by electrolyzing PbO obtained from waste lead acid batteries in alkaline solution. The sodium ionic exchange membrane is used to avoid HPbO_2^- being oxidized to PbO_2 on the anode. The new system is not only low energy consuming, but also beneficial to improving the lead recovery efficiency. Furthermore, the new recovery process realizes the circulation of the waste electrolyte, avoiding emission of lead effluent. The effect of concentration of NaOH solution on the cell voltage of the electrolytic bath was studied. Experimental results indicate that the cell voltage of electrolytic bath is 1.23 V, the current efficiency is 99.9%, the lead recovery efficiency is 99.8% and the energy consumption reaches $317 \text{ kWh ton Pb}^{-1}$ at a current density of 20 mA cm^{-2} .

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1. Introduction

The lead acid battery has been widely used in automobile, energy storage and many other fields and domination of global secondary battery market with sharing about 50% [1]. Since the positive electrode and negative electrode active materials are composed of $\text{PbO}_2/\text{PbSO}_4$ and Pb/PbSO_4 , lead is the most important raw material of lead acid batteries. In 2010, the world's annual refined lead output reached up to 9.3 million tons, of which about 86% was consumed in the manufacture of lead acid batteries [2,3]. Recycling lead from wasted lead acid batteries is related to not only the sustainable development of lead-acid battery industry, but also the reduction of the lead pollution to the environment.

In recent decades, to reduce the secondary contamination of lead vapors and lead dust caused by pyrometallurgical recovery process, researchers have developed some new methods of hydrometallurgical recovery technology [4–6]. Because both PbSO_4 and PbCl_2 have low solubility in acid environment, people have to use toxic HBF_4 or H_2SiF_6 to dissolve PbO for preparing $\text{Pb}(\text{BF}_4)_2$ or PbSiF_6 solution to obtain the electrolytic lead [7–9]. However, on the one hand, the high electrolytic bath voltage of 2.2–2.9 V in acidic $\text{Pb}(\text{BF}_4)_2$ solution and the formation of by-product PbO_2 on the anode result in high energy consumption of 550–750 kWh ton Pb^{-1} [4,7]. On the other hand, toxicity and causticity of $\text{HBF}_4/\text{H}_2\text{SiF}_6$ solution restrict its

industrialization application. In addition, some researchers electrolyze the lead compound to obtain lead powder by adopting solid phase electrolysis [10]. However, this method has the disadvantage of low lead recovery rate because the electrolytic Pb powder is easy to oxidize in the atmosphere. For these reasons, the existing hydrometallurgical methods have not accepted commercial approval.

Generally, PbO can be considered as a kind of alkaline metal oxide, so it has limited solubility in diluted NaOH solution. However, it has been observed that PbO can easily react with NaOH to form $\text{Na}[\text{Pb}(\text{OH})_3]$ or NaHPbO_2 in hot and concentrated NaOH solution, leading to a high solubility of 110 g L^{-1} so as to make it possible to reclaim metallic Pb in alkaline solution.

In this paper, we report a new lead recycling technology from waste lead acid batteries, in which the alkaline solution containing PbO is directly electrolyzed to produce metallic lead of high purity by using sodium ionic exchange membrane to separate the catholyte and anolyte to avoid HPbO_2^- being oxidized to PbO_2 on the anode. The lead recovery system takes the advantage of the lower theory decomposition voltage of PbO in alkaline solution and simple technological process as well as the possibility of waste electrolyte recycling.

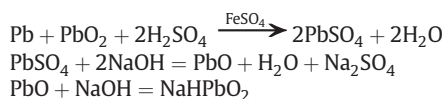
2. Experimental

The powders of crushed positive and negative plates from the waste lead acid batteries and sulfuric acid were placed in a three-neck flask in which the ferrous sulphate was added as a catalyst and reductant to accelerate the reaction to obtain lead sulfate precipitation [11]. The lead sulfate was dissolved in high concentration of NaOH

* Corresponding authors. Tel./fax: +86 10 64449332.

E-mail addresses: jqpan@mail.buct.edu.cn (J. Pan), sunyz@mail.buct.edu.cn (Y. Sun).

solution at 80 °C to obtain alkaline solution of NaHPbO₂ as catholyte. The above reactions can be expressed as:



The electrolytic bath was separated into cathode and anode areas by Nafion 2030 membrane (Fig. 1). The dimension of the electrolytic cell was 12 cm × 20 cm × 6 cm. The Cu foil and porous nickel foam with the same area of 10 cm × 15 cm were used as cathode and anode, respectively. The distance from anode to membrane and membrane to cathode was 0.1 cm and 1.2 cm, respectively. Both volumes of anolyte chamber and cathode chamber were all 10 cm × 15 cm × 2 cm. The NaHPbO₂ and NaOH solution were pumped into the cathodic and anodic chambers by using two pumps respectively and both solution flow rates were 600 ml min⁻¹. The electrolysis temperature was controlled at 85 °C. The current efficiency was calculated by the ratio of the weight of metallic lead obtained on the cathode to the theoretical value. The polarization tests were carried out in a cell of three electrode system. A Cu foil was used as working electrode, a pure electrolytic lead plate as auxiliary cathode and a Hg/HgO electrode as reference electrode.

A LAND2001A battery test system and a CSU300 electrochemical workstation were used to control electrolytic process and record the data during the electrolysis process. The X-ray powder diffraction (XRD) patterns were collected by means of a Rigaku D/max2500VB2+/PCX diffractometer with a Cu anticathode (40 kV, 200 mA), a scan rate of 10° min⁻¹ and a scan range (2θ) from 10° to 90°. The morphology and granularity of the product were examined by means of FSEM (Cambridge S250MK3) observation.

3. Results and discussion

When PbO is electrolyzed in alkaline solution, the possible electrode reactions of the cathode and anode can be expressed as:

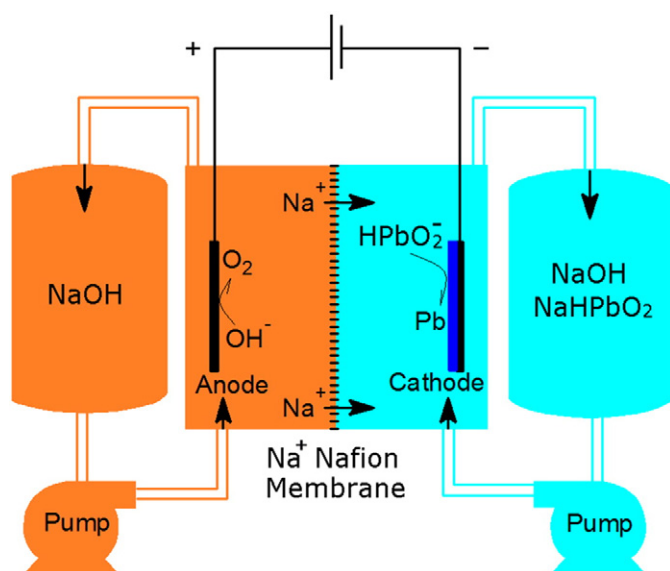


Fig. 1. The diagram of the electrolysis bath.

For the cathodic process, the potential of lead is more positive than that of hydrogen, so the main reaction on the cathode is the lead deposition rather than hydrogen evolution. However, for the anodic process, the HPbO₂⁻ is easier to lose electron than OH⁻ to form PbO₂. Herein, we propose a new technology to solve this problem by using sodium ionic exchange membrane to separate NaHPbO₂–NaOH catholyte from pure NaOH anolyte, resulting in that only OH⁻ could be oxidized to O₂ on the anode. So Eqs. (1–2) and (1–3) are the main reactions for the cathode and anode, respectively, and the whole reaction can be expressed as:



The potential difference between cathodic (1–2) and anodic (1–3) reactions in alkali is 0.938 V, which is much lower than that for the electrolysis of PbSiF₆ in acid solution (1.229 – (–0.126) = 1.355 V), so the electrolysis of the alkaline PbO solution is much lower energy consuming. After the electrolysis reaction finished, a certain amount of NaOH equivalent to the consumed PbSO₄ was added to the catholyte and then the solution was cooled down to precipitate Na₂SO₄ which has low solubility in concentrated NaOH solution. Half of the obtained NaOH solution was reused to dissolve PbSO₄ again and the other half was added to the anodic chamber to balance NaOH anolyte consuming during the electrolysis process.

Fig. 2 represents the galvanostatically polarization potential vs. time curve at different cathodic current density. As shown in Fig. 2 that all curves are relatively stable and only 0.135 V polarization potential is increased when the current density increases from 5 mA cm⁻² to 100 mA cm⁻², implying that the low polarization potential of lead cathode is beneficial to reducing the electrolytic cell voltage.

Fig. 3A displays the effect of concentration of NaOH electrolyte on the cell voltage. It can be seen that the lowest cell voltage of 1.46 V is achieved when the concentration of NaOH in anolyte is 20% and that in catholyte is 30%. It is believed that the cell voltage depends mainly on the conductivity of electrolyte and the voltage drop of the ionic membrane. Higher concentration of NaOH anolyte is helpful for Na⁺ to migrate from the anode chamber to cathode area, thus achieving a low cell voltage. However, the extra high concentration of NaOH anolyte (35%) leads to cell voltage increase instead because of dehydration of the membrane with higher NaOH concentration. So the appropriate concentration of NaOH in catholyte should be controlled at 15–20%, and that in anolyte at 30%. Under this condition, a relatively low cell voltage of 1.45–1.49 V can be obtained.

Fig. 3B exhibits the constant current electrolysis curves at different current density. It can be seen from Fig. 3B that the cell voltage rises gradually with increasing the current density. When the current density reaches 80 mA cm⁻², a severe polarization phenomenon appears

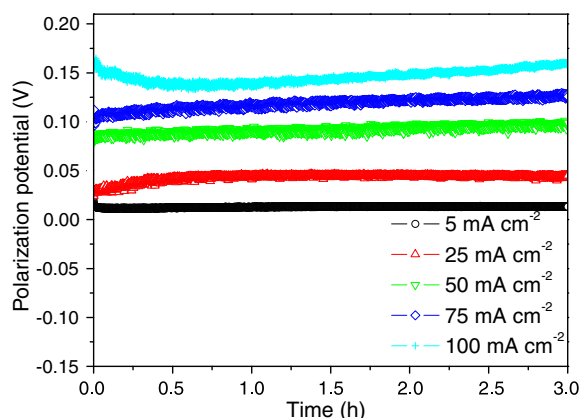


Fig. 2. Cathodic polarization potential vs. time curves of the Pb cathode at different current density.

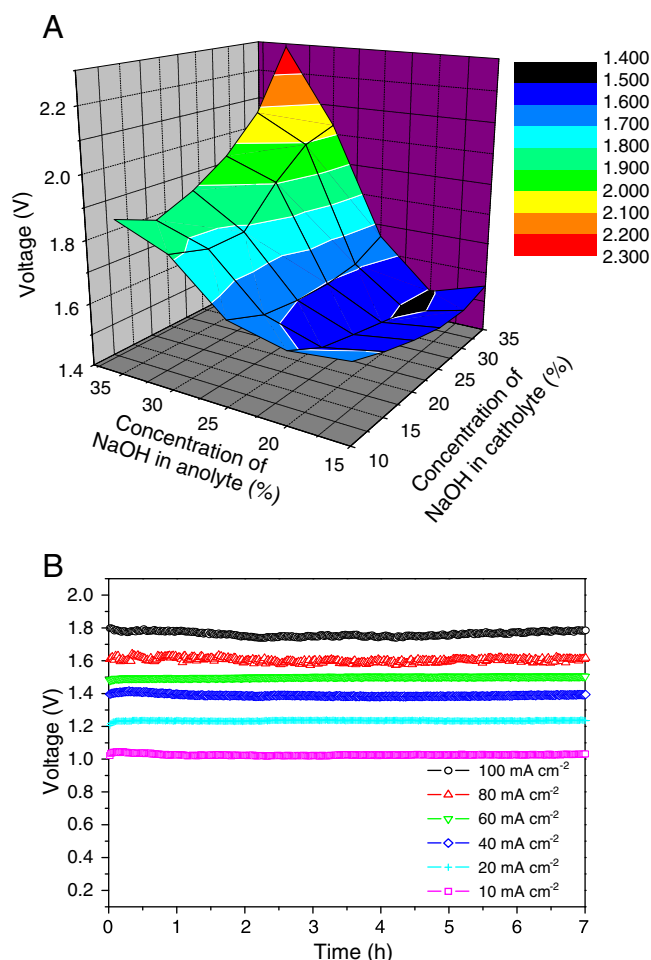


Fig. 3. The effects of concentration of NaOH (A) and current density (B) on the cell voltage. The current density in A is 60 mA cm⁻² and the numbers of electrolysis times are 30. For panel B, the concentration of NaOH in anolyte is 30% and concentration in catholyte is 20%, respectively.

on the electrolytic curve and the cell voltage is as high as 1.61 V. According to the Faraday law, the high cell voltage will result in a high energy consumption. However, the low current density would lead to a low production efficiency. In order to guarantee a high yield of time and space and a low energy consumption, an appropriate current density should be controlled between 20 and 60 mA cm⁻², corresponding to a cell voltage between 1.23 and 1.49 V, a current efficiency of 99.9%, and the energy consumption between 317 and 384 kWh ton⁻¹. The gravimetric analysis result shows that the recovery rate of Pb can reach up to 99.8% in the electrolytic process.

Fig. 4A exhibits the FSEM photograph of the electrolytic product. As shown in the figure, the product presents a dense crystal structure, just containing a small quantity of dendritic lead grains on the surface. The XRD pattern of the obtained sample is shown in Fig. 4B. It can be seen that the characteristic diffraction peaks of (111), (200), (220), and (311) crystal lines of the electrolytic product all conform to those peaks of standard JCPDF# 65–2873 card for metallic lead. It is obvious that the electrolytic product is pure lead. However, a minor diffraction peak of PbO at 16.44°, which results from the oxidation of a little metallic lead after electrolysis in the atmosphere, is also observed.

4. Conclusions

The high purity metallic lead can be obtained directly through electrolyzing an alkaline solution containing PbO which is obtained from

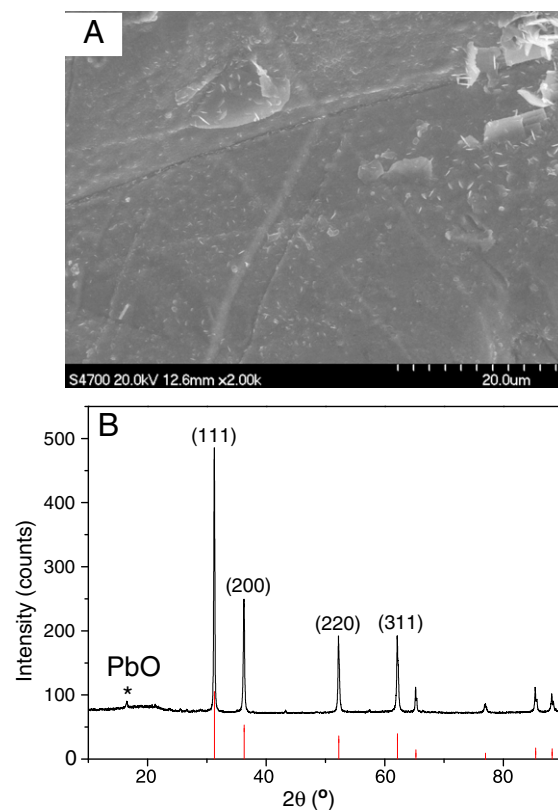


Fig. 4. The XRD patterns (A) and FSEM photos (B) of the produced lead.

waste lead acid batteries by catalytic reaction and desulfuration, while the by-products is only O₂. The sodium ionic exchange membrane is used to separate the anolyte from the catholyte to avoid HPbO₂⁻ being oxidized to PbO₂ on the anode. The cell voltage for the new process is between 1.23 and 1.49 V and the energy consumption between 317 and 384 kWh ton⁻¹, corresponding to current density between 20 and 60 mA cm⁻². The current efficiency is as high as 99.9% and the electrolytic lead recovery rate reaches up to 99.8%. In addition, the new recovery process avoids the emission of lead effluent by means of the recycling of the waste electrolyte. Therefore, it is a lead recovery process of low energy consumption and environmental friendliness.

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